PHOTOIONIZATION MASS SPECTROMETRIC STUDIES OF THE COMBUSTION INTERMEDIATES CH_2OH AND CH_3O*

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I. INTRODUCTION

The radical species CH_3O and CH_2OH are believed to play important roles as intermediates in the combustion of hydrocarbon fuels.[1,2] Recently, absorption spectra in the visible-UV have been observed for both species,[3-10] primarily using laser methods. Accurate experimental vibrational frequencies are known for both species, and a rotational analysis (and hence geometric structure) is known for CH_3O. Despite this intensive study, the heats of formation of these species are still somewhat uncertain.

Cruickshank and Benson[11] studied the iodination reaction

$$CH_3OH + \rightarrow CH_2OH + HI\,,$$

and obtained an endothermicity of 24.6±1.5 kcal/mol. Utilizing this value, Golden and Benson[12] compute $\Delta H°_{f_{298}}$ (CH_2OH) = -4.2±1.5 kcal/mol. However, Golden and Benson also cite Buckley and Whittle,[13] who studied the corresponding bromination reaction, and inferred an endothermicity of <4.2 kcal/mol. From this latter observation, one can deduce $\Delta H°_{f_{298}}$ (CH_2OH) ≤ -8.3 kcal/mol. In order to give some weight to the bromination data, Golden and Benson[12] chose $\Delta H°_{f_{298}}$ (CH_2OH) = -6.2±2.5 kcal/mol. The compilation of Glushko et al.[14] selects $\Delta H°_{f_{298}}$ (CH_2OH) = -4.8±2.4 kcal/mol as the middle range of several experiments, three of which are based on an incorrect ionization potential of CH_2OH (vide infra).

For $\Delta H°_f$ (CH_3O), most recent papers cite the experiments of Batt and co-workers.[15-17] Batt and Milne[16] determined the bond energy of CH_3O-NO by kinetic measurements (assuming no reverse activation energy) to be 41.8 kcal/mol. Using $\Delta H°_{f_{298}}$ (CH_3ONO) = -16.0 kcal/mol from Silverwood and Thomas,[18] they obtained $\Delta H°_{f_{298}}$ (CH_3O) = 4.2±0.7 kcal/mol. Subsequently, Batt and McCulloch[17] obtained $\Delta H°_{f_{298}}$ (CH_3O) = 3.8±0.2 kcal/mol from the kinetics of dimethyl peroxide pyrolysis. Glushko, et al.,[14] surprisingly not citing Batt and co-workers, arrive at 3.1±1 kcal/mol from an examination of other sources.

At this point, it is convenient to introduce some *ab initio* calculations which have focused on the difference in stabilities of CH_2OH and CH_3O. Saebo et al.[19] show that CH_3O is 4.1 kcal/mol more stable than CH_2OH at the Hartree-Fock level (6-31 G** basis sets). However, when electron correlation is included, CH_2OH becomes more stable. At the MP3/6-31 G** level, and including zero point energies, CH_2OH is 5.0 kcal/mol more stable than CH_3O. At this level, the barrier to isomerization ($CH_3O \rightarrow CH_2OH$) is found to be 36.0 kcal/mol. Later, Colwell[20] obtained an almost identical result - CH_2OH more stable by 5.86 kcal/mol, and a barrier height of 37.29 kcal/mol - using CI (singles and doubles) with a Davidson correction and a double zeta plus polarization basis set. However, in the recent calculation by Curtiss et al.[21] at the G2 level (more correlation) CH_2OH is found to be 8.8 kcal/mol more stable than CH_3O. Our prior analysis of experimental data would lead to a difference of (8.4 - 10.4) ± 2 kcal/mol. A previous experimental estimate of this quantity by Batt et al.[22] arrived at 7.5 kcal/mol.

The adiabatic ionization potential (I.P.) of a molecular species is the difference between the heats of formation of that species and the corresponding cation. Hence, if the heat of formation of the desired

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cation is well known, and its adiabatic I.P. can be obtained, it offers an alternative route to the heat of formation of the neutral species. It turns out that ΔH°_f (CH_2OH^+) is rather well known from photoionization measurements[23] of the appearance potential of CH_2OH^+ from CH_3OH and C_2H_5OH. These measurements yield $\Delta H^\circ_{f_0}$ (CH_2OH^+) $\geq 172.0 \pm 0.7$ and ≤ 171.7 kcal/mol, respectively. The adiabatic ionization potential of CH_2OH has been obtained in a photoelectron spectroscopic study by Dyke and co-workers,[24] who obtained I.P. (CH_2OH) = 7.56 ± 0.01 eV. We shall re-examine this result in the experiments to be described below. Combining $\Delta H^\circ_{f_0}$ (CH_2OH^+) and I.P. (CH_2OH), we obtain $\Delta H^\circ_{f_0}$ (CH_2OH) $\leq -2.3 \pm 0.7$ kcal/mol, or $\Delta H^\circ_{f_{298}}$ (CH_2OH) $\leq -3.9 \pm 0.7$ kcal/mol.

In the case of CH_3O, the heat of formation of its cation is very much in question. Dyke[25] reports 7.37 $\pm$ 0.03 eV as the adiabatic I.P. of CH_3O. Taking ΔH°_f (CH_3O) $\approx 4.0 \pm 1$ kcal/mol (vide supra), we infer ΔH°_f (CH_3O^+) ≈ 174 kcal/mol. (We ignore for the moment the distinction between $\Delta H^\circ_{f_0}$ and $\Delta H^\circ_{f_{298}}$). By contrast, Burgers and Holmes[26] deduced ΔH°_f (CH_3O^+) = 247 ± 5 kcal/mol from a somewhat complicated argument. First, they showed that the "CH_3O^+" ions previously believed to be produced by dissociative ionization of CH_3ONO and $(CH_3)_2O$ were really CH_2OH^+, and consequently earlier (lower) heats of formation of CH_3O^+ based on these measurements were invalid. They then prepared CH_3O^+ by charge reversal (starting with CH_3O^-). Upon measuring the metastable peak from the unimolecular decomposition process

$$CD_3O^+ \rightarrow DCO^+ + D_2 ,$$

they found that it had the same shape (i.e., the same kinetic energy release) as that from $CD_3OD^+ \rightarrow [D_2COD^+] \rightarrow DCO + D_2$. Consequently, they argued that the transition state for formation of the DCO^+ metastable was the same, whether starting from CD_3O^+ or D_2COD^+, and that this transition state was "at or close above the enthalpy of formation of CD_3O^+." They measured the appearance potential of the metastable DCO^+ peak from CD_3OD (15.1 ± 0.2 eV) which, together with literature values for ΔH°_f (CD_3OD) and ΔH°_f (H), leads to a heat of formation of the transition state of 247 ± 5 kcal/mol. More recently, Ferguson, et al.[27] made an estimate of ΔH°_f (CH_3O^+) which provided some support for the value deduced by Burgers and Holmes. The argument is again somewhat involved, but they infer ΔH°_f (CH_3O^+) = 245 ± 6 kcal/mol.

If ΔH°_f (CH_3O) is ~4 kcal/mol, then these latter inferences regarding ΔH°_f (CH_3O^+) imply I.P. (CH_3O) $\cong$ 10.5 eV, very different from Dyke's 7.37 ± 0.03 eV. The major purpose of the current research was to resolve this huge discrepancy.

II. EXPERIMENTAL ARRANGEMENT

The experimental apparatus is a vacuum ultraviolet (VUV) photoionization mass spectrometer. It consists of a VUV light source (in this case, the emission spectrum from an electric discharge in molecular hydrogen), a 3-m VUV monochromator, a chamber where the gas to be studied is crossed by the light exiting from the monochromator, some ion optics and a quadrupole mass spectrometer. The apparatus operates windowless, with differential pumping, and hence can be utilized to much higher photon energies. The VUV light is monitored by a bare photomultiplier, while the ions strike another bare multiplier and are pulse counted. The data consist of ion intensity (normalized to light intensity) as a function of wavelength, which we refer to as the photoion yield.

Experiments of this sort for stable gases can be performed routinely. Transient species present more serious problems, because the number density is much smaller, and the methods of producing these transient species may generate additional noise. We have prepared CH_3O and CH_2OH by the reaction of F atoms with CH_3OH. Several previous studies have shown that H atom abstraction occurs at both the C and O position. McCaulley et al.[28] have recently studied this reaction, and review earlier results.

A schematic drawing of the apparatus for generating transient species *in situ* near the region of photoionization has been described previously.[29] In order to distinguish between CH_2OH and CH_3O, we have used isotopic variants of methanol, particularly CD_3OH and CH_3OD. With CD_3OH, CD_3O^+ occurs at m/e = 34, and CD_2OH^+ at m/e = 33; with CH_3OD, CH_3O^+ occurs at m/e = 31, CH_2OD^+at m/e = 32.

III. EXPERIMENTAL RESULTS

A. The F + CD_3OH reaction

1. CD_2OH^+, M33

The photoion yield curve of M33, presumed to be CD_2OH^+ (CD_2OH), displays at least 3 sloping step-like features. They correspond in energy (approximately) to the positions of the peaks in Dyke's[25] photoelectron spectrum of CD_2OH. Hence, the dominant ionization process appears to be direct ionization. The half-rise of the first step occurs at 1644.3 ± 3 Å ≡ 7.540 ± 0.006 eV, which we take to be the adiabatic I.P. of CD_2OH. Dyke gives 7.55 ± 0.01 eV for this quantity. In Dyke's spectrum (and also in ours), there is a weak peak (background in ours) at ~7.4 eV. In order to distinguish between a still lower threshold and a hot band, we performed a simple quasi-diatomic Franck-Condon calculation, assuming harmonic behavior and a frequency (presumed to be C-O^+) of 1610 cm^{-1}, taken from Dyke. From the relative peak intensities, we calculate a change in bond length of 0.12 Å. Whangbo, et al.[30] have computed a contraction of 0.13 Å in the C-O bond length between CH_2OH and CH_2OH^+, in excellent agreement. Alternatively, if we assign the $0 \rightarrow 0$ peak as $0 \rightarrow 1$, we can calculate the intensity expected at the $0 \rightarrow 0$ position. The intensity of the weak peak at ~7.4 eV is about a factor 5 lower than the predicted intensity and the overall fit for higher peaks becomes much poorer. Hence, this weak feature is attributed to a hot band.

2. CD_3O, M34

The photoion yield curve of M34, presumed to be CD_3O^+ (CD_3O), displays a broad underlying "background," but an abrupt increase in ion yield occurs at 1155.9 ± 0.9 Å ≡ 10.726 ± 0.008 eV. We take this to be the adiabatic I.P. of CD_3O. The underlying background has about the same shape as CD_2OH^+ from CD_2OH, but is about a factor 20 weaker. A possible source of this background may be the F + CD_3OH reaction itself, where some CD_2OD may be formed. Beyond threshold, one can observe sloping, step-like features with intervals of ~2400 cm^{-1}.

B. The F + CD_3OD, CH_3OD and CH_3OH reactions.

Some of these experiments are still in progress; consequently, these are preliminary results. The F + CD_3OD reaction yields CD_3O, and photoionization produces CD_3O^+ with essentially the same onset as obtained in the F + CD_3OH experiment. However, in the F + CD_3OD experiment CD_2OD is also formed, and its subsequent ionization yields ion intensity at the same mass, but at lower energy. Hence, CD_3O is identified as an increase in the photoion yield at m/c = 34, above that due to CD_2OD^+.

An adiabatic onset for CH_3O^+ is not observed at the wavelength expected in the F + CH_3OD and F + CH_3OH experiments. Some ionization at m/e = 31 is observed at shorter wavelength (higher photon energy). From zero point energy considerations,[21] the adiabatic I.P. of CH_3O should be the same as CD_3O, within about 0.001 eV. Hence, the absence of CH_3O^+ at the expected wavelength implies that it is unstable. In fact, HCO^+ is observed in this case, in the approximate abundance expected for the decomposition $CH_3O^+ \rightarrow HCO^+ + H_2$. The adiabatic I.P. of CH_2OH is found to be 1641.5 ± 1.3 Å ≡ 7.549 ± 0.006 eV.

IV. DISCUSSION OF RESULTS

A. CH_2OH - CH_2OH^+

The adiabatic I.P. of CH_2OH obtained in this study (7.549 ± 0.006 eV) is very nearly the same as that reported by Dyke[24,25] (7.56 ± 0.01 eV) by photoelectron spectroscopy. Taking $\Delta H°_f$ (CH_2OH^+) ≤ 172.0 ± 0.7 kcal/mol, we deduce $\Delta H°_f$ (CH_2OH) ≤ -2.1 ± 0.7 kcal/mol, or $\Delta H°_{f_{298}}$ (CH_2OH) ≤ -3.7 ± 0.7 kcal/mol, which is at the upper end of the range given in the Introduction.

B. CD_3O - CD_3O^+

The I.P. for CD_3O obtained here (10.726 ± 0.008 eV) is obviously very different from Dyke's[25] 7.37 $\pm$ 0.03 eV. Dyke's experiment consisted of measuring the photoelectron spectrum of the pyrolysis products from dimethyl peroxide. The spectrum is suggestive of a blurred CH_2OH spectrum, but further speculation on our part is unwarranted. If we take $\Delta H^\circ_{f_{298}}$ (CH_3O) = 4.0 ± 1 kcal/mol, then ΔH°_f (CH_3O) = 5.9 ± 1 kcal/mol, and ΔH°_f (CH_3O^+) becomes 253.2 $\pm$ 1 kcal/mol (251.2 $\pm$ 1 at 298 °K). This latter value is within the range deduced by Burgers and Holmes[26] (247 $\pm$ 5) and estimated by Ferguson, et al.[27] (245 $\pm$ 6 kcal/mol).

C. CH_3O^+ - CD_3O^+

Our failure to observe CH_3O^+, although CD_3O^+ was observed, suggests that zero point energy differences or tunneling could account for their relative stabilities. According to *ab initio* calculations,[21,31] the ground state CH_2OH^+ potential energy surface is a singlet, whereas that of CH_3O^+ is a triplet. Ionization of CH_3O will strongly favor formation of CH_3O^+, over CH_2OH^+, by Franck-Condon considerations. However, CH_3O^+ will initially be formed more than 3 eV above the ground state of CH_2OH^+, and above the thermochemical threshold for formation of $HCO^+ + H_2$ (which also represents a singlet surface). One can expect that there will be some crossing between the triplet CH_3O^+ surface and the singlet surface. Spin-orbit interaction should permit some mixing between the triplet and the singlet surface, and hence the crossing will become an avoided crossing, resulting in a potential barrier. In its lowest vibrational state, CD_3O^+ appears to be stable to decomposition by barrier penetration (on a time scale of $\sim 10^{-5}$ sec) whereas CH_3O^+ is not. We look forward to the results of future *ab initio* calculations, which may clarify this point.

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